

**Argonne National Laboratory**

**FACTORS INFLUENCING DROSS FORMATION  
IN THE FUSIBLE SEALS OF  
THE EBR-II ROTATING PLUGS**

**by**

**W. E. Ruther**

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EBR-II Project

January 1970



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ABSTRACT

The factors influencing the rate of dross formation in the fusible seals of the EBR-II rotating plugs were studied in the laboratory using a rotating cylinder in a beaker of the fusible alloy Bi-42 wt % Sn.

The results indicated that dross formation in a simple rotating system may be a complex process. A single, linear oxidation rate was found for only those few experiments in which the oxidation product did not mechanically interact with the rotor.

In the more general case, the mechanical interaction of the dross with the rotating system resulted in substantially greater oxidation rates after an initial period of operation. The oxidation rate during the initial period was shown: (a) to be linearly related to circumferential velocity of the rotor in the range of velocities examined in the EBR-II (0-100 in./min) and (b) to be independent of the rotor size. The secondary oxidation rate, reached after about 600 min, was linearly related to velocity for a given rotor, but was dependent on rotor size.

No large effect of alloy composition on the secondary oxidation rate was found when the tin content was varied (37-47 wt %) or when aluminum was added. Indium (4 wt %) proved effective in reducing the rate of dross formation in the basic alloy. However, little benefit was derived from the indium addition when sodium (at the level found in the actual seal trough) was added to the alloy containing 4 wt % In.



## I. INTRODUCTION

Several sodium-cooled reactors have used one or more circular gas-seal troughs during indexing a single fuel-handling device to each reactor-grid position. The function of the seal is to prevent inleakage of air into the inert gas atmosphere over the chemically reactive sodium while permitting the required mechanical movements of the reactor cover. The EBR-II uses a Bi-42 wt % Sn alloy (melting at  $\sim 140^{\circ}\text{C}$ ) in the gas-seal troughs of the rotating plug. Figure 1 shows a section through a fusible seal of the rotating plug.

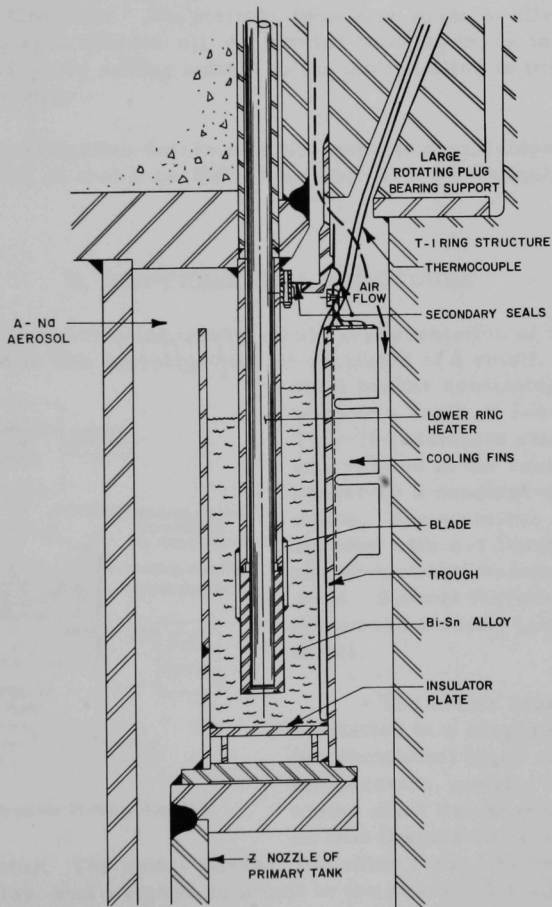


Fig. 1. Section through Fusible Seal of EBR-II Rotating Plug



The original reactor design incorporated secondary baffle seals on the air side to maintain a chemically inert atmosphere over both gas-liquid and liquid-metal interfaces. However, the baffles were ineffective and permitted access of air to the outer liquid-metal interface. Moreover, the number of fuel transfers has increased greatly as a result of the revised program for the EBR-II as a fast-flux test reactor in the Liquid Metal Fast Breeder Reactor (LMFBR) development program. Consequently, large amounts (over 1000 lb in 1969) of a black oxidation product of the Bi-Sn alloy are formed during fuel-handling operations. This dross impedes the movement of the blade through the trough and laboriously must be removed through a tiny port. The problem has been investigated by Blumenthal *et al.*,<sup>1</sup> and by Crothers.<sup>2</sup> Suggestions have been made to alleviate the difficulty by using a silicone oil, or similar fluid layer, on the air-exposed Bi-Sn alloy and/or by adding indium to the molten alloy to improve its oxidation resistance.

This investigation determines the important variables in the rate of dross formation, so that a realistic appraisal of the proposals might be made.

## II. EXPERIMENTAL PROCEDURE

Figure 2 shows a laboratory-scale representation of the dressing apparatus used in this investigation. It consisted of a small, stainless steel beaker containing the sample alloy to a depth of 3-4 in. A solid, Type 304 stainless steel cylinder was rotated in the center of the beaker by a constant-speed gear motor. The stainless surfaces were abraded with wet Durite (240 grit) abrasive sheets before each experiment. A short thermocouple was immersed directly into the liquid metal.

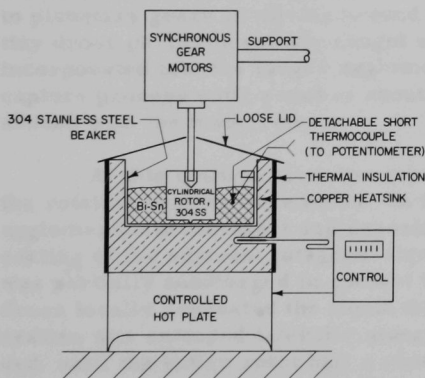


Fig. 2. Laboratory-scale Dressing Apparatus

raising the motor. The entire beaker, including rotor, thermocouple, and frozen seal alloy, was weighed as a unit to the nearest 0.1 mg on a 1-kg-capacity analytical balance. Two sizes of beakers were used: the smaller rotor (of 1.0-in. OD) was used with a 2.5-in.-ID beaker; the larger rotor (of 1.8-in. OD) was used with a 3.3-in.-ID beaker. No attempt was made to limit the access of air to the Bi-Sn surface.

The entire beaker was thermostatted in a snug-fitting copper (or aluminum) block at the desired temperature, usually  $180 \pm 2^\circ\text{C}$ . The motor shaft was keyed into the rotor so that it could be detached by simply



### III. DATA AND RESULTS

Data were collected on the influence on dross formation of rotor velocity, temperature, wetting, and alloy composition. In the sections that follow, these data are examined individually for applicability to the fusible seals of the EBR-II rotating plugs.

#### A. General Observations

A thin, protective coating formed over the molten Bi-Sn surface as it was brought to 180°C. An undisturbed beaker of molten alloy, held at 180°C for 22 hr, gained only 11 mg of oxygen (0.4 mg/cm<sup>2</sup> of liquid-metal surface). Crothers and Cooper<sup>3</sup> held a beaker of the molten alloy for over a year, and only slight thickening of the protective coating occurred. Thus, the extensive dross formation experienced in the tests to be described here was the direct result of rotor motion. No correction in weight gain was necessary for the slight oxidation during the brief heating and cooling periods with no rotation.

The shear zone in the liquid metal was localized at or near (within ~0.05 in.) the rotor surface when rotation was started. As the rotor turned, tiny particles of dark dross appeared on the surface of the alloy in the shear zone. These tiny particles were spun on their own axes by the action of the shearing metal. They were also carried around with the rotor at a velocity inversely related to their diameters. The system appeared similar to planetary gears revolving around a sun gear. Thus, the newly formed, tiny dross particles quickly caught up to larger dross particles and were incorporated into the larger agglomerates. These continued to grow by this capture process until a unit of about 1/4-in. diameter was slowly moving around with the main rotor.

At this critical size, two modes of disengaging the dross group from the rotating system were noted. In the more common (drossing) mode, the agglomerate broke apart and deposited most of the dross on top of the oxide coating of the adjacent, stagnant liquid metal. The remainder of the dross was partially submerged in contact with the rotor surface. The submerged dross locally separated the liquid metal from the rotor surface. This separation was extended laterally along the rotor surface as the rotation continued, until the entire rotor had a continuous band of dross rotating slowly and separating the rotor from the surface of the liquid metal. Fresh corrosion product was constantly formed at the base of the separation, and also at the interface between the rotating ring of dross and the molten alloy. Thus, a dross-filled "V" notch was formed adjacent to the rotor, as shown schematically in Fig. 3, after about 8 hr of operation. A further consequence of the drossing mode of operation was that all the initially immersed rotor surfaces, even the horizontal bottom in some cases, acquired a coating of black dross. Because of the large disturbed surface of liquid metal involved, this mode led to an acceleration in the oxidation kinetics.



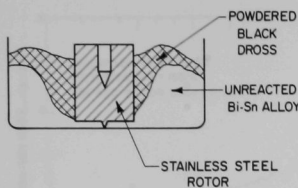


Fig. 3. Section through Beaker after Eight Hours of Operation in Dressing Mode

time at a value substantially less than that reached in the previously described dressing mode. Figure 4 shows that little or no black dross was formed on the surface.

The powdered, black corrosion product formed in the dressing mode looked like dross obtained from the seal trough of the EBR-II. The total weight of the experimental black powder was roughly greater by two orders of magnitude than the measured weight gain due to the oxygen reaction. This increased weight was also in agreement with EBR-II experience, because it had been shown<sup>2</sup> that reactor dross consisted of up to 80 wt % unoxidized metal and that oxygen was present largely as tin oxide.

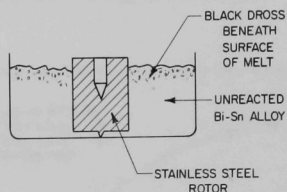


Fig. 4. Section through beaker after Eight Hours of Operation in Submerged Mode

## B. Influence of Rotor Velocity on Dross Formation in Bi-Sn Alloy

The four curves in Fig. 5 illustrate the influence of circumferential rotor velocity at 180°C on the oxidation (dross formation) of Bi-42 wt % Sn alloy. The EBR-II seals may be moved at certain fixed velocities between 20 and 87 in./min.

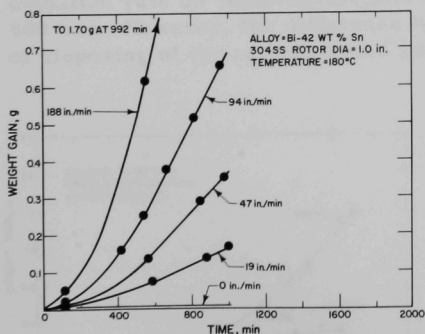


Fig. 5. Oxidation of Fusible Seal Alloy

A secondary, linear oxidation rate was reached for each rotational velocity after an induction period which ranges for 100 to 400 min. This induction period correlated well with the time required for the vertical surface of the rotor to become coated with adherent black dross.

Figure 6 shows that secondary oxidation rates (at ~1000 min) have a nearly linear relationship with rotor circumferential velocity.



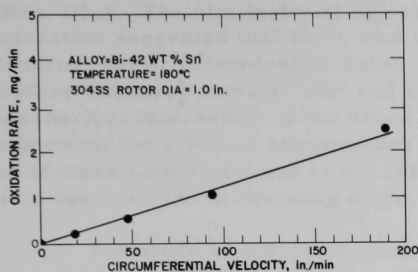


Fig. 6. Secondary Oxidation Rates as a Function of Circumferential Velocity

The oxidation rate for the first exposure periods (~120 min) were taken as representative of a "clean" system, i.e., before the mechanical interaction of the dross with the rotating system became significant. Figure 7 shows the linear relationship found with rotor velocity for velocities up to ~100 in./min. Increased slippage between the rotor and alloy may account for the departure from linearity at higher rotor velocities. The magnitude of the secondary oxidation rate (see Fig. 6) for a given velocity was approximately four times the value during the induction period.

Only one experiment was performed at 180°C with the larger rotor and beaker, and the results are shown in Fig. 8. This was the first test in which no external dross was formed. The data from this test fit well with initial oxidation rates determined for the smaller rotor (see Fig. 7).

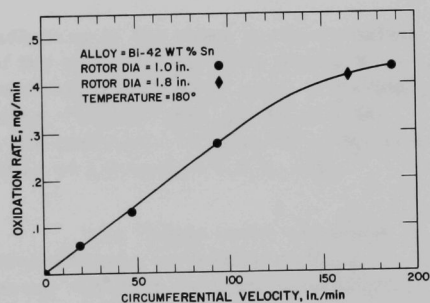


Fig. 7. Initial Oxidation Rates as a Function of Circumferential Velocity

### C. Temperature Dependence of Oxidation Rate

The data presented in Figs. 8 and 9 indicate a strong dependence of oxidation rate on temperature after 400 min. However, the difference in behavior was related to the two modes of disposing of the agglomerated corrosion product, as described in

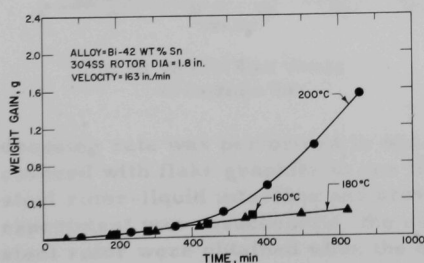


Fig. 8. Effect of Temperature on Oxidation Rate in Large Rotor

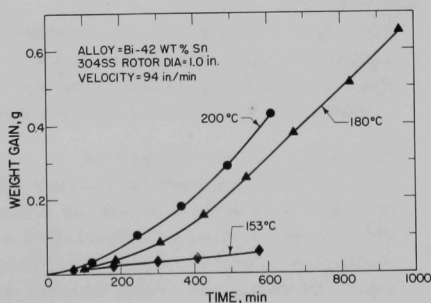


Fig. 9. Effect of Temperature on Oxidation Rate in Small Rotor



Sect. III.A. The similarity of oxidation rates during the initial period of operation suggested that there was no strong effect of temperature on the tendency toward chemical oxidation. However, a comparison of the secondary oxidation rates at 180° and 200°C (see Fig. 9) indicated that the mechanical interaction of the dross with the rotating system magnified somewhat the effect of temperature on the drossing rate. The latter case is of more direct interest to the actual reactor-seal problem, because the seal operates in the drossing mode.

The mode of corrosion-product disposal was dependent on the interplay of the mechanical stresses with physical properties of the alloy, and these properties were temperature-dependent. Although a detailed study of these parameters is beyond the scope of this investigation, the effect of wetting of the rotor by the liquid metal was especially pronounced and should be noted here.

#### D. Wetting of the Rotor

The appearance of black dross adhering to the rotor surfaces below the liquid level suggested that wetting of the rotor by the alloy played a significant role in the transition to the secondary oxidation rate. A Teflon (not wetted by the alloy) and a copper rotor, "tinned" with Bi-42 wt % Sn and solder flux, were tested to evaluate the extremes. Figure 10 compares the results of these experiments with those of a standard 1.0-in.-dia, Type 304 stainless steel rotor.

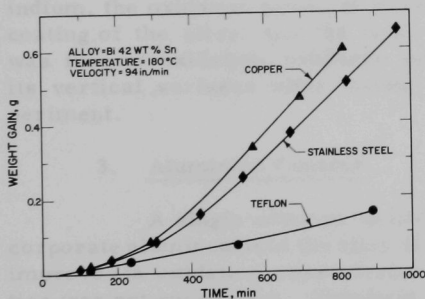


Fig. 10. Effect of Rotor Wetting on Oxidation Rate

The Teflon rotor showed a much slower transition; in fact, it never reached the usual secondary oxidation rate. This rotor had much less dross adhering to its vertical surface than did the copper or stainless steel rotors.

The secondary oxidation rate was reached somewhat faster for the copper rotor than for the Type 304 stainless steel, although the actual slope was only slightly greater than that obtained with the steel rotor.

An experiment to reduce the drossing rate was performed in which the surface of the liquid metal was covered with flake graphite to see if it could be worked down the stainless steel rotor-liquid metal interface and provide a low-friction shear surface. This experiment was unsuccessful; the usual oxidation kinetics for a stainless steel rotor were obtained when the dross formed under the graphite layer.



## E. Effect of Alloy Composition on Dross Formation

Variations in concentrations of the alloy components (tin, indium, aluminum, and sodium) affect the rate of dross formation to the degree shown below.

### 1. Tin Content

A series of experiments was performed to determine the effect of tin concentration on drossing rate for the binary Bi-Sn system. As

TABLE I. Secondary Oxidation Rates<sup>a</sup> of Bi-Sn Alloys

Tin Concentration, wt %	Linear Rate, mg/min
37	1.4
42	1.1
47	1.4

<sup>a</sup>Slope at 900 min; 180°C; 94-in./min velocity; a 1.0-in. rotor.

shown in Table I, the variations in the secondary oxidation rates were not large for a range of 37-47 wt % Sn with the minimum at the eutectic composition.

of 1 and 4 wt % In to the Bi-42 wt % Sn alloy. During the 4 wt % addition of indium, the oxidation products were incorporated under the surface coating of the alloy, and the rotor was free of oxidation products on its vertical surfaces after the experiment.

### 3. Aluminum Content

A single attempt to incorporate aluminum into the alloy to improve its oxidation characteristics was not successful. Aluminum (1 wt %) was added at high temperature (680°C) to the eutectic Bi-Sn alloy. Extensive amounts of solid aluminum intermetallic compound were present at the dross test temperature of 180°C. The dross formed hard, metallic-appearing agglomerates, about the shape of small grains of rice. The particles stuck together to form a hard crust over the alloy. Oxidation weight gains were taken only three times during a total of 365 min; the three values fell exactly on the normal Bi-42 wt % Sn curve.

### 2. Indium Content

Indium additions to the Bi-42 wt % Sn alloy have been proposed as a method for reducing dross formation<sup>2</sup> because of the improved oxidation resistance to the ternary alloy. Figure 11 shows the effects on the drossing kinetics of additions

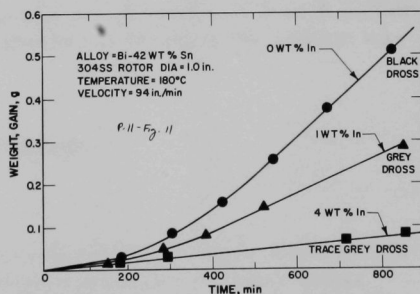


Fig. 11. Effect of Indium Additions on Oxidation Rate



#### 4. Sodium Content

The sodium concentration of the alloy in the seal trough of the EBR-II has been reported to be approximately 0.2 wt %.<sup>2</sup> Accordingly, alloys containing this concentration of sodium were prepared in an inert-atmosphere glovebox by melting and stirring. No solid intermetallic compound was noted after about 5 min of stirring at  $\sim 180^{\circ}\text{C}$ . Figure 12 shows the results of this sodium addition on the oxidation kinetics of the Bi-42 wt % Sn and the Bi-40.3 wt % Sn-4 wt % In alloys.

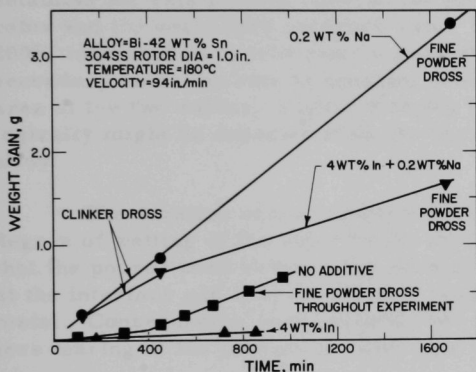


Fig. 12. Effect of Sodium Additions on Oxidation Rate

used up at that time. The benefit gained by the presence of 4 wt % indium was small during that portion of the experiment in which the sodium was present.

The experiment was continued overnight, so fewer data points than usual were taken. The induction period was essentially eliminated, and the dross formed stuck together to form hard "clinkers" during at least the first 400 min of operation. The oxidation rates were also substantially higher than those for the same alloy without sodium.

At the end of the exposures ( $\sim 1700$  min), the dross being formed was the usual fine black powder, suggesting that the sodium had been preferentially oxidized and was essentially

#### IV. DISCUSSION

##### A. General

The results of this investigation indicated that dross formation in a simple rotating system may be a complex process. A single linear oxidation rate was found for only those few experiments in which the oxidation product did not mechanically interact with the rotor.

In the more general case, the mechanical interaction of the dross with the rotating system resulted in substantially greater oxidation rates after an induction period. The oxidation rate during the initial period was shown to be linearly related to the circumferential velocity of the rotor in the range of velocities of interest in the EBR-II (0-100 in./min) but independent of the rotor size. During the initial period after reactor startup,



varying temperatures (160-200°C) had only a small effect on the oxidation rate. Limited data suggested that the temperature effect was larger after the drossing mode had been established.

The secondary oxidation rate, reached ~600 min after the drossing mode began operation, was related linearly to velocity for a given rotor but was dependent on rotor size. The dross, mechanically introduced below the initially submerged rotor surfaces, permitted oxygen access to a much larger liquid-metal-air interface. Insufficient data have been obtained to establish the relationship between the physical dimensions of the submerged rotor and the secondary oxidation rate. However, a single set of data at 200°C indicated an approximately proportional relationship between the secondary oxidation rate at constant velocity and the vertical, submerged area of the two rotors. Figure 3 shows that this sort of relationship logically might be expected from the physical appearance of the oxidized alloy.

The duration of the induction period was inversely related to the degree of wetting of the rotor by the liquid metal. It had been suggested that the poorer bond between the solid and liquid resulted in more slippage at the interface and less mechanical force being transmitted to the liquid metal. Consequently, less shearing was required in the liquid metal, and less tearing of the protective oxide film occurred.

No large effect of alloy composition on the secondary oxidation rate was found for variations in tin content (37-47 wt %) or for addition of aluminum. Indium (4 wt %) was effective in reducing the rate of dross formation for the basic alloy, but it was much less useful when small amounts of sodium were present in the liquid metal.

## B. Application to EBR-II

The simple experimental apparatus used in this investigation differed in several aspects from the actual reactor seal trough. For example, the radii of curvature for the blade and wall of the reactor seal differed by only ~1%, whereas for the beaker experiments the ratio of the larger to the smaller radii was usually 2.5. The larger ratio tended to concentrate the mechanical shear in the liquid at or near the surface with the smaller radius; in the actual trough, it might be expected that shear would divide more evenly between the blade and wall. However, the linear relationship between velocity and oxidation rate suggests that the same total dross would be formed, independent of the division of the shear forces. The same linear relationship indicates that no optimum velocity exists for the operation of the seals, and the total dross should depend solely on the distance traveled.



A more serious problem in the scale-up of the experimental results is the influence of the depth to which the blade is immersed. The beaker experiments show that the secondary oxidation rate could be correlated with the formation of a milled-in coating of dross on the immersed surfaces of the rotor. Cooper's experience<sup>3</sup> with a model of the EBR-II seal trough on a much larger scale has shown the presence of dross on the immersed surface of the blade after extensive operation. The secondary oxidation-rate factor has not been determined for this larger model, and it is not known for the actual reactor seal. However, the rate-increase factor could be much larger for the actual blade than for these experiments, in view of the greater immersed area of the blade as compared with results using the small experimental rotor.

A consequence of the presence of dross on the immersed surfaces of the reactor blade is the possibility that silicone oil, or similar fluid proposed as an oxidation retardant on the air side, would creep along the dross coating. In this way, small amounts of oil might be introduced into the inert-gas phase of the reactor vessel and transmitted as a vapor to high temperature stainless steel components. Surface carburization of these components would thus become possible.

Unfortunately, none of the variables studied suggested a feasible way to achieve improvement by an order of magnitude in the rate of dross formation in the reactor seal troughs. Since the blade is presumably already coated with dross, none of the possible techniques for prevention of mechanical interaction of the dross with a clean blade would be expected to be useful.

The value of indium additive to the alloy was so sharply reduced by the presence of sodium at trough concentration that the added expense of the indium would not be justified, unless the sodium aerosol could be trapped elsewhere.

#### ACKNOWLEDGMENTS

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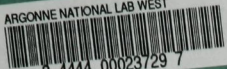


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